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Dated 30 July 2003

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16JUL02 E733289-1 D01091
P01/7700 0.00-0216323.6

Request for grant of a patent

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13 JUL 2002

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Cardiff Road
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1. Your reference — MN 1605 GB

2. Patent application number *(The Patent Office will fill in this part)* — 0216323.6

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

JOHNSON MATTHEY PUBLIC LIMITED COMPANY
2-4 COCKSPUR STREET
TRAFALGAR SQUARE
LONDON SW1 5BQ

Patents ADP number *(if you know it)* — 536268007

If the applicant is a corporate body, give the country/state of its incorporation — GB

4. Title of the invention — ALLOY

5. Name of your agent *(if you have one)* — IAN CARMICHAEL WISHART

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

JOHNSON MATTHEY TECHNOLOGY CENTRE
BLOUNTS COURT
SONNING COMMON
READING RG4 9NH

Patents ADP number *(if you know it)* — 399141001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* — YES

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	0
Description	7
Claim(s)	1
Abstract	1
Drawing(s)	4 +4 Ry

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Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	ONE
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature I C WISHART Date 12 July 02

I C WISHART

12. Name and daytime telephone number of person to contact in the United Kingdom

MRS F E STRANGE 0118 924 2125

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DUPLICATE

ALLOY

This invention relates to alloys of iridium, in particular to alloys of iridium with low amounts of alloying elements and uses thereof.

Iridium is a member of the platinum group of metals and has a variety of applications including automobile catalysts, electrodes for industrial electrolysis, crucibles for crystal growth, thermocouples, rocket motor parts, glass making and spark plugs. It has several attractive properties including a very high shear modulus at room temperature and elevated temperature strength second only to tungsten among the refractory metals. It is also thought to be the most corrosion resistant of all metals.

However, despite these benefits there are some disadvantages. Its mechanical properties are sensitive to certain low level impurities and strain rate and it also exhibits a ductile-brittle transition. Due to the rarity of its occurrence in nature its price per gram is of the same order as platinum and furthermore its density is the second highest of all elements. Finally, although compared to the refractory metals its resistance to oxidation is excellent, it nevertheless does exhibit a significant weight loss at elevated temperature under oxidising conditions.

As a result of its scarcity and difficulty in maintaining metal purity during manufacture, the metallurgy of iridium is poorly understood. Indeed little work, relative to that done on alloying of platinum for instance, has been carried out to investigate the effect of alloying on properties. However, the alloying with some elements has been investigated by different workers. Oak Ridge National Laboratories in the USA have been responsible for developing one alloy, DOP-26 based on Ir-0.3W +Th, for radioisotope thermoelectric generator casings used to supply power to spacecraft. Tungsten has been shown to increase the alloy re-crystallisation temperature of iridium by 400°C at >2wt% addition, which makes control of microstructure during hot working, much simpler. Thorium has been shown to promote ductility below the normal ductile/brittle transition zone, although its radioactivity is a major disadvantage when considering this alloy for normal commercial applications. Certain Rare Earth elements,

Ce, Y and Lu have also been investigated, and Ce has been found promote similar properties to Th, although less pronounced. ORNL have developed a new alloy range based on Ir-0.3W with low levels of Ce + Th.

US 3,918,965 describes a binary alloy of iridium with 0.3 to 1 wt% hafnium. Improvements in physical properties are claimed.

Work has been limited in respect of alloying iridium with platinum group metals (PGM). Rhodium additions, up to a maximum of ca. 10wt%, have been shown to improve oxidation resistance, ductility and formability. Application of 40%Rh-Ir to novel rocket nozzles was reported in the early 1990's. Ternary alloys have also been long considered for pen nibs, and electrodes. The advent of long life spark plugs has re-invigorated interest in the potential of iridium alloys. Rhodium additions have been found to be beneficial, with 40wt% being best for oxidation resistance. Additions of 10wt% of both platinum and palladium also improve the oxidation resistance of iridium, although not as effectively as rhodium. Al, Si, Cr, Mo and W were found to be ineffective.

EP0866530 A1 discloses ternary and quaternary alloys of iridium, rhodium and at least one of rhenium and ruthenium. Low levels of Re and Ru, either singly or combined, significantly reduce the oxidation loss of an alloy at 1100°C for 30hours, compared to pure iridium. The presence of rhodium is essential, as Re and Ru have little or no effect when combined with iridium alone.

Although prior attempts to improve the physical and mechanical properties of iridium by alloying have met with some success, there remains a need for further improvements.

In accordance with the present invention, an iridium alloy comprises iridium and one or more base metals chosen from Ce, Sc, Lu, Re, Co, Ni, Mo, Hf, Zr, Y, W, Ta, Nb and Ti, or one or more platinum group metals chosen from Pt, Rh, Pd and Ru, or any combination thereof; wherein each base metal comprises between 0.01 and 0.5 wt% of

the alloy; and wherein each platinum group metal comprises between 0.1 and 5 wt% of the alloy.

The alloys of the present invention show enhanced physical and mechanical properties over pure iridium. Typically, alloys may comprise up to 2wt% in total of base metals and up to 10wt% of platinum group metals other than iridium itself, although alloys with greater amounts of alloying elements are not considered to be outside the scope of the present invention.

In a first embodiment, the alloy comprises iridium and Pt, or iridium, W and Pt. In tensile tests, these alloys demonstrate a considerable increase in elongation to failure compared to pure iridium. In some cases, elongation to failure is increased two-fold and more.

In an alternative embodiment, the alloy comprises iridium and Zr, or iridium, W and Zr. In measurements of stress rupture times at elevated temperatures, these alloys may outperform pure iridium by a factor of twenty or more. Creep rates at high temperature are also significantly reduced. Furthermore, W and Zr may also retard grain growth at high temperature, with small additions of both W and Zr being found to reduce the rate of grain growth at high temperature by a factor of two compared to pure iridium.

In a further alternative embodiment, the alloy comprises iridium, Rh, W and Zr or iridium, Rh, Pt, W and Zr. Significant reduction in weight loss under high temperature oxidising conditions is found for these alloys, when compared to pure iridium.

The enhanced physical and mechanical properties of the alloys of the present invention make them suitable for use in many high temperature or load bearing applications. For example, they may be used in ignition applications i.e. as components in spark-plugs or as crucibles or other equipment in chemical and glass applications where high strength, low creep rate and good oxidation resistance are required. Other applications include electrodes, heat shields and rocket nozzles. The foregoing examples

merely serve to illustrate the many potential uses of the present alloys, and as such, are not intended to be limiting in any way.

The alloys may be manufactured by known methods and fabricated into any suitable physical form. Improvements in elongation to failure, or ductility, make the alloys particularly suitable for drawing into wires however, tubes, sheets, grains, powders or other common forms are also contemplated. The alloys may also be used in spray coating applications.

The invention will now be described by way of example only and with reference to the following drawings in which;

Figure 1 is a bar chart comparing the mean elongation at room temperature of two alloys according to the present invention with pure iridium;

Figure 2 is a bar chart comparing the stress rupture time at elevated temperature of four alloys according to the present invention with pure iridium;

Figure 3 is a bar chart comparing the rate of grain growth at elevated temperature of four alloys according to the present invention with pure iridium, and;

Figure 4 is a graph comparing the measured weight loss of two alloys according to the present invention with pure iridium.

EXAMPLE 1

Elongation to failure

The alloys detailed in table 1 below were prepared by argon arc melting.

Table 1.

Alloy	Composition /wt%
1	Pt 0.20, balance Ir
2	Pt 0.20, W 0.30, balance Ir

Alloys 1 and 2 were hot drawn into wires of 1.8mm diameter, and subjected to tensile testing with a gauge length of 51mm and a cross head speed of 5mm/minute. The results are shown in Fig. 1. Additions of Pt and/or W at the ppm level significantly improved the room temperature mechanical properties of the alloys. Although ultimate tensile strength was found to only be improved marginally, elongation to failure, in the case of alloy 2, increased by 117% relative to similar wires of pure iridium.

EXAMPLE 2

Stress rupture

The alloys detailed in table 2 below were prepared by argon arc melting

Table 2.

Alloy	Composition /wt%
3	Zr 0.07, balance Ir
4	Zr 0.02, W 0.30, balance Ir
5	W 0.05, balance Ir
6	Zr 0.02, W 0.05, balance Ir

Alloys 3-6 were hot rolled into sheets and tensile sample blanks formed by spark erosion machining. These were then surface ground to a thickness of nominally 1.8mm. The gauge length of each sample blanks was 30mm. Stress rupture times were measured at a temperature of 1400°C and stress of 75MPa. Results are shown in Fig. 2. Significant improvements in stress rupture times were found for all alloys compared to pure iridium, with ppm levels of Zr (alloy 3) or Zr and W (alloy 6) being most effective. Although not shown in Fig.2, creep rates at elevated temperature were also reduced, in some cases by as much as a factor of 16 compared to pure iridium.

EXAMPLE 3

Grain growth retardation.

Alloys 3-6 as detailed in table 2 above, were hot rolled into sheet of nominally 3.5mm thickness . The alloys were held at 1550°C for 400 hours and grain size measurements made. This was done using an optical microscope. The number of grains intersecting a line traversing the polished and etched section were counted and averaged over the cross sectional thickness. Results are shown in Fig. 3. Grain growth was reduced for all alloys compared to pure iridium, with ppm levels of Zr and W (alloy 6) showing a halving of grain size.

EXAMPLE 4

Oxidation weight loss

The alloys detailed in table 3 below were prepared by argon arc melting.

Table 3.

Alloy	Composition /wt%
7	Rh 2.50, W 0.30, Zr 0.07. balance Ir
8	Rh 2.50, Pt 2.50, W 0.30, Zr 0.07, balance Ir

Alloys 7 and 8 were hot drawn into wires of between 0.6 and 1.2mm and their weights monitored while being held at 1000°C for 200 hours. Results are shown in Fig. 4. The weight loss of both alloys was approximately 4 times less than that for pure iridium, over the duration of the test, and approached that which was found for a commercial 10wt%Rh-Ir alloy.

EXAMPLE 5

Engine tests

Alloys 7 and 8, as detailed in table 3 above, were formed into spark plug electrodes. During testing in a high performance car engine over a period of 175 hours,

the electrodes were found to erode at a similar rate to commercial 10wt%Rh-Ir alloy electrodes, and at a much reduced rate compared to pure iridium electrodes.

CLAIMS

1. An iridium alloy, the alloy comprising iridium and one or more base metals chosen from Ce, Sc, Lu, Re, Co, Ni, Mo, Hf, Zr, Y, W, Ta, Nb and Ti, or one or more platinum group metals chosen from Pt, Rh, Pd and Ru, or any combination thereof; wherein each base metal comprises between 0.01 and 0.5 wt% of the alloy; and wherein each platinum group metal comprises between 0.1 and 5 wt% of the alloy.

2. An alloy according to claim 1, the alloy comprising iridium and Pt or iridium, W and Pt.

3. An alloy according to claim 1, the alloy comprising iridium and Zr or iridium, W and Zr.

4. An alloy according to claim 1, the alloy comprising iridium, Rh, W and Zr or iridium, Rh, Pt, W and Zr.

5. An electrode comprising an alloy according to any preceding claim.

6. A spark plug comprising an electrode according to claim 5.

7. The use of an alloy according to any of claims 1 to 4 in a high temperature application.

8. The use of an alloy according to any of claims 1 to 4 in a load bearing application.

ALLOY

Abstract

An iridium alloy comprises iridium and one or more base metals chosen from Ce, Sc, Lu, Re, Co, Ni, Mo, Hf, Zr, Y, W, Ta, Nb and Ti, or one or more platinum group metals chosen from Pt, Rh, Pd and Ru, or any combination thereof. Each base metal comprises between 0.01 and 0.5 wt% of the alloy and each platinum group metal comprises between 0.1 and 5 wt% of the alloy. The alloys show enhanced physical and mechanical properties compared with those of pure iridium, and are thus useful in high temperature and load bearing applications.

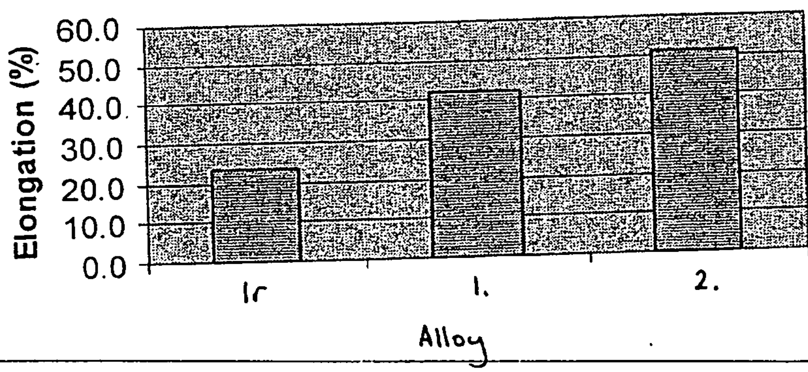

Fig. 1

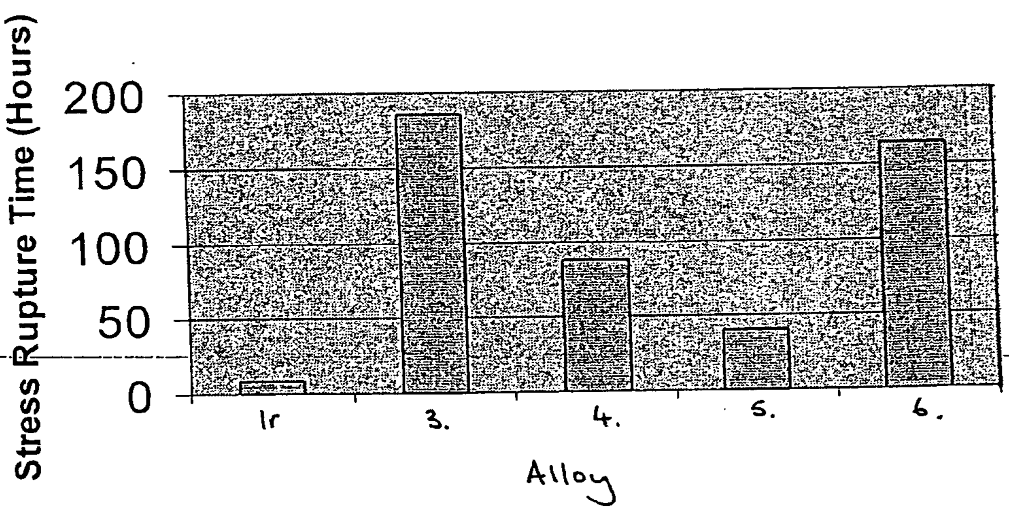

Fig. 2

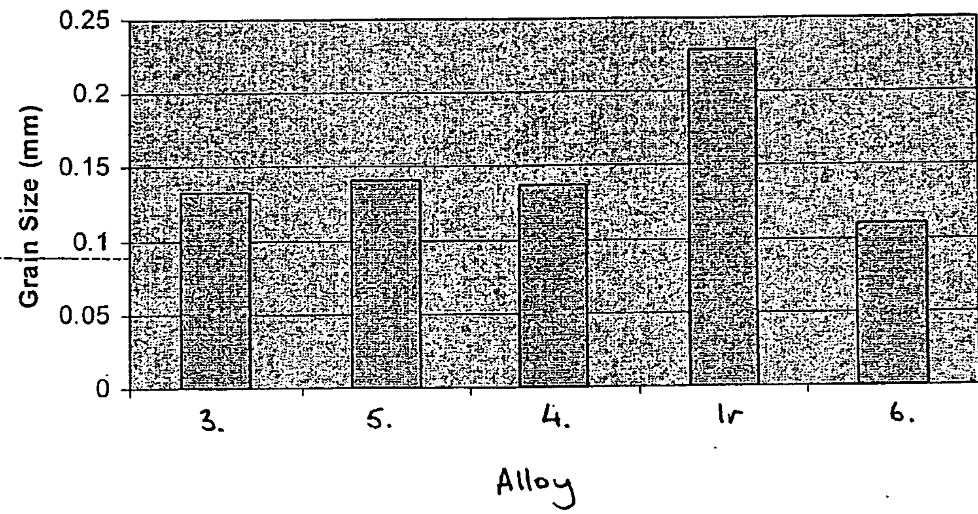

Fig. 3

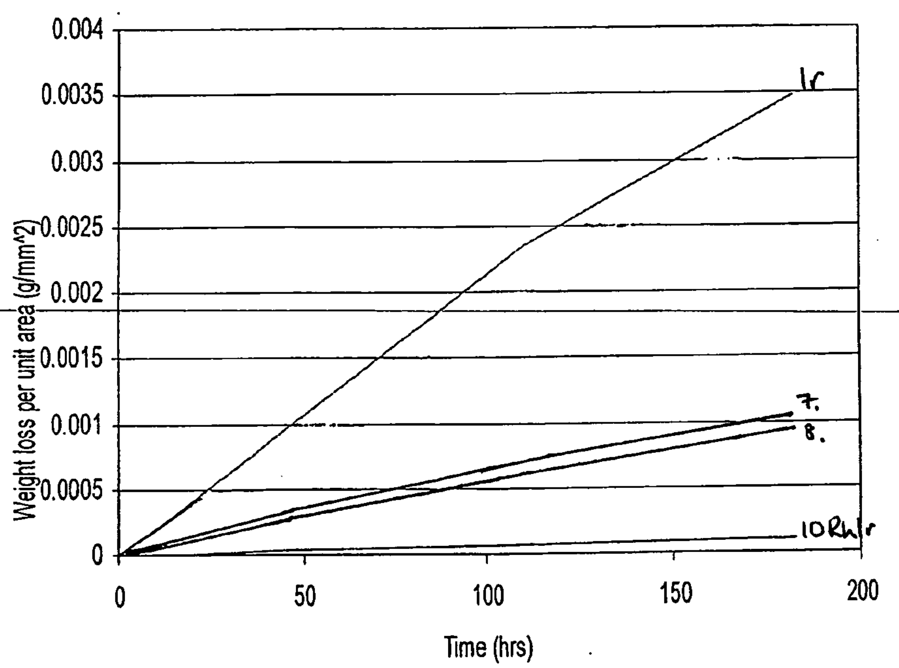
Weight loss per unit area (g/mm^2)
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0
50
100
150
200
Time (hrs)
Ir
7.
8.
10Rh/Ir

Fig. 4